

THE STABLE HIGH TEMPERATURE CO₂-ACCEPTOR. THERMOANALYTICAL STUDY

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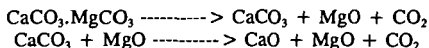
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The studied high temperature CO₂-acceptor intended for the persistent removal of CO₂ from chemical reactors fits special requirements. It is characterized by the high CO₂ capacity and durability; its structure stability is held on the cyclic variation of inner stresses produced by the consequence of carbonation-decarbonation. The acceptor which consists of CaO and MgO (periclase) has been prepared from dolomite. Experimental data demonstrate CaO phase to work as CO₂-acceptor and MgO one to form a rigid framework, which provides the stability to the grains structure. The volume of CaCO₃ phase formed exceeds twice the initial volume of CaO phase. However, this effect is eliminated due to the periclase framework: acceptor grains do not demonstrate any expansion on CaCO₃ formation.

The CO₂-acceptor was developed with the properties allow using it on new effective technology of the methane steam reforming process (ASMR). The main peculiarity of this technology is continuous CO₂ remove from the reaction zone of ASMR by means of solid acceptor which continuously circulates through this zone.

The acceptor should demonstrate sufficient high activity on interaction with CO₂. Besides the acceptor must have a high attrition resistance (AR). Finally it must be stable enough to both these parameters. The most suitable materials for producing CO₂-acceptor is dolomite CaCO₃.MgCO₃.

At temperature ranges of ASMR-process dolomite is decomposed by two stages:



Formed due to stage (1) MgO is inactive because of sintering after formation. An active component of acceptor is CaO, which is formed as a result of reversible reaction (2). The direct using of dolomite as a CO₂-acceptor is impossible mainly because of phase transition which accompanied both indicated reactions.

Disordering of crystal lattice leads to lowering of AR. So the proceeding of the low temperature stage (1) induces the decrease of initial value of AR for dolomite from about 40% to zero. Stage (2) is accompanied by the transition CaCO₃ phase to CaO and vice versa.

The dolomite destruction due to phase transition made impossible a realization of prospective technology of coal-gasification known as "CO₂-acceptor process". Simultaneously an ability of dolomite to lose activity due to sintering was also found out. All these data were obtained on semi commercial plant.

According to our purposes the grain of the acceptor must include a stable and chemical inert framework, distributed in all volume of grain. Active component (CaO) is disposed in the space cells of the framework.

MgO was chosen as a matter for creating a framework because of its ability to sintering and formatting inactive and stable periclase. Further it would be expedient to choose dolomite as a MgO-containing material, which includes CaO also.

During our experiments we have developed a method of dolomite treatment which allows producing CO₂-acceptor, not having the lacks typical for dolomite.

The above discussed practical-important properties of studied solids were determined using the next methods: 1) activity A_{CO₂} was determined as CO₂ in carbonated samples; 2) the value of AR was determined in the device, simulated the air-lift at a linear velocity equaled 25-30 m/s.

The stability of samples was characterized by changing the values of A_{CO_2} , AR and by the specific surface in the long runs with intermittent cycles of decomposition (1100-1200K) and carbonation (by 900-950K). Total duration of the tests was 100h, a number of cycles was near 50.

The fresh acceptor has a high value of AR (80%), which near twice higher than for fresh dolomite. In test the AR value was lowered during 10-30h, then it remained near constant and equaled to that for fresh dolomite. The AR values for carbonated and decomposed samples differed insignificantly. It means that for the acceptor the transition of $CaCO_3$ to CaO does not affect its structure.

The A_{CO_2} value was in fact constant changed within 25 to 27 percent. This is in good agreement with the almost constant value of the specific surface, which is equal to 2.3-2.6 m^2/g for decomposed samples and to 0.4-0.8 m^2/g for carbonated samples.

For the study of formation of CO_2 -acceptor we have chosen two thermoanalytical methods: thermogravimetry and dilatometry. This permitted us firstly to register the value of mass changing and the rate of this process and secondly to register the grain-framework response to the consequence variation the volume of the active phase.

The work was carried out by microbalance "Sartorius" and dilatometer "Netzsch" adapted by us for the work in different gases flow at the temperatures from ambient to 1000°C. The same programs and conditions of experiments were used for different methods. The data on mass change and elongation are given in dimensionless form $\Delta m/m$ and $\Delta l/l$.

First of all, the behaviors of natural dolomite and acceptor in course of the cyclic $CaCO_3$ - CaO transitions were compared. In this series of experiments, the carbonate decomposition in air flow was studied only. Dilatometric curves for heating of samples are given in Fig. 1 as dependencies of temperature coefficient of linear expansion on the temperature. Dilatogram of the first decarbonation of natural dolomite (curve 1) indicates the great extent of contraction in the temperature range higher than 600°C and, especially, higher than 700°C, where decomposition of calcium carbonate takes place. At the second decarbonation (curve 2) the considerable contraction peak in the range of 400-600°C has been observed which corresponds to decomposition of magnesium carbonate. Further in the not large temperature interval (from 600 to 700°C) the grain structure is evidently supposed by calcium carbonate phase, but its decomposition at temperature higher than 700°C induces endless contraction of grain which indicates to the destruction of sample.

Dilatogram of the first decarbonation of acceptor (curve 1a) shows not so significant effect of decreasing temperature coefficient in the temperature range corresponding to decomposition of magnesium carbonate and not so large contraction peak in the temperature range higher than 700°C corresponding to the decomposition of calcium carbonate.

As the cycling proceeds, the first effect disappears really, and the second decreases. On the fourth cycle (curve 2a) we obtain at almost whole temperature range the positive temperature coefficient of thermal expansion decreasing at temperature - higher 800°C only. Thus cycling the acceptor (two-phase system) leads to stabilization of the grain framework, but cycling the natural dolomite (one-phase system) induces destabilization of its structure and then destruction of the grain.

Then the comparative study of acceptor samples different in intensity of natural dolomite treatment which transforms it to CO_2 acceptor was carried out. These intensities are represented below in arbitrary units (a.u.).

In Fig. 2 the thermogravimetric curves for acceptors obtained by mild and by severe treatment of dolomite are compared (5 and 18 of a.u. correspondingly). Previously these samples were decarbonated, after that they were linearly heated and cooled in CO_2 flow. The curve for sample 5 is continuous line, the curve for sample 18 is noted by stars. It can be seen that the interaction with CO_2 begins at quite low temperature (from 300 to 400°C), but it proceeds not so quickly and follows up to relatively high temperature. The thermogravimetric curve for sample 18 is displaced to high temperatures essentially (approximately by 200K) as related to the curve for sample 5. This is connected evidently with the fact, that transforming natural dolomite into acceptor is followed by the scaling acceptor structure, - decreasing its porosity and, may be, section of transport pores and other effects inducing decrease of rate of interaction

with CO_2 . Thermogravimetric curve for sample 18 exceeds the temperature of thermodynamic equilibrium for calcium carbonate decomposition before ending the carbonation. Nevertheless it can be seen that capacities of both samples are close enough and quite large: the quantity of CO_2 uptake exceeds 30% of mass of the sample containing MgO and CaCO_3 . Decomposition of carbonate proceeds in both samples with high and close rates. The decrease of temperature returns the samples into the region of carbonate formation. Thermogravimetric curves for cooling testify the high rate of carbonation, but exceed the saturation at more low level than those for heating. This fact is induced, may be, by sintering CaO becoming real at this quite high temperature after CO_2 isolation.

Consider now the response of grain structure to calcium carbonate formation and decomposition. In Fig. 3, one from thermogravimetric curves for heating and cooling the sample 18 in CO_2 flow shown in previous figure and corresponding dilatogram, the scale for ordinate of which is increased approximately hundred times are presented. This permits us to use the common ordinate y for representation dilatogram (dotted line) and thermogravimetric curve and to compare the both curves. At heating dilatogram character corresponds to thermal expansion of the sample. The similar curve in the bottom part of the figure corresponds to thermal contraction at cooling. Thermogravimetric curve for heating demonstrates at 600°C the beginning of calcium carbonate forming. At 750°C - approximately 30% of calcium oxide transforms into carbonate. The total volume of reacting and forming phases increases approximately by 30%, however dilatogram does not indicate any expansion of sample.

On the contrary at 700°C in spite of forming the carbonate with considerable rate deceleration of thermal expansion and then contraction of sample is observed the latter finishes in the temperature region corresponding to decomposition of carbonate and isolation of CO_2 .

During the cooling of the sample at temperature about 870°C thermogravimetric curve indicates increasing the sample mass - approximately by 10% (30% of CaO forms carbonate).

There is insignificant splash in dilatogram - this effect corresponds approximately to thermal expansion of the sample at heating by 10-12 K. Thus the carbonate formation does not induce practically any expansion of acceptor. This result testifies apparently that there is some functional and space separation of two phases in acceptor. Components of these phases (CaO and MgO) constituted previously one-phase structure of dolomite. It may be thought that after segregation of phases magnesium oxide transforms into stable inert form - periclase. The latter forms grains framework keeping its stability and sitting the second phase - calcium oxide which is the acceptor really so that volume variations of the latter do not lead to the excess inner framework stresses. Suggested scheme is apparently simplified.

Consider Fig. 4 permitting to coincide thermogravimetric (top figure) and dilatometric (bottom figure) curves for heating in air the acceptors 5 and 18 subjected previously to treatment with CO_2 at high pressure, i.e. saturated completely. The dotted lines correspond to the sample 5. It can be seen that sample capacities are very high and close to one another (the calculation with regard to carbonated sample is given). Thermogravimetric curves of carbonate decomposition also coincide practically. It can be seen not large displacement (not more than 1%) in the region where decomposition of magnesium carbonate takes place - about 500°C . Analogous displacement can be observed in dilatogram for sample 18 shown in bottom figure and for some other samples. The fact that quite small quantity of decomposed magnesium carbonate can induce dilatometric effect permits us to suppose that activation of MgO can proceed on interphase boundaries where the reaction of calcium oxide can catalyze the surface layers of periclase. As thermogravimetric curves for decarbonating samples 5 and 18 practically coincide, the corresponding dilatometric effects appear to be different: sample 18 indicates more less contraction than sample 5. Evidently this is connected with larger durability and rigidity of its framework.

While during heat treatment of samples in carbon dioxide flow or in air effects of volume increase are practically absent the contraction of samples is often observed. Evidently contraction of samples is induced by a complex of reasons, which require further investigation.

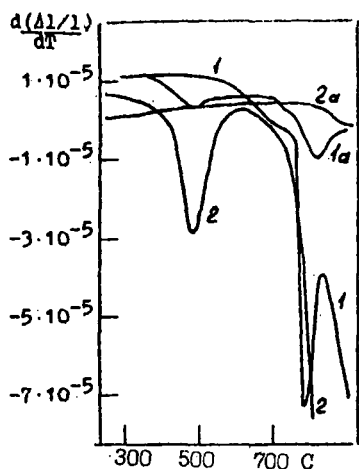


Figure 1. The dependencies of the linear expansion coefficient on temperature for cyclic heating of natural dolomite (1 and 2) and CO₂ acceptor (1a and 2a)

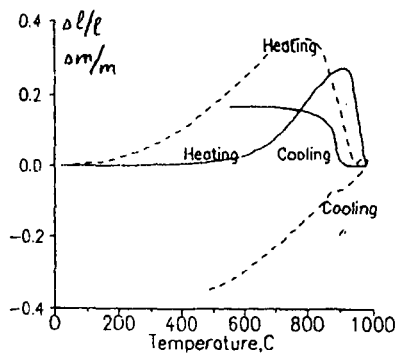


Figure 3. The comparison of the thermogravimetric and dilatometric (dotted line) curves of the heating and cooling in the CO₂ flow for acceptor 18. The y axis scale (elongation) is enlarged about 100 times.

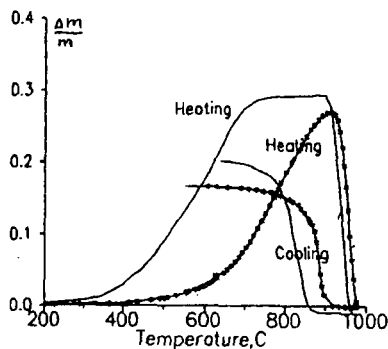


Figure 2. The thermo-weight curves of the heating and cooling in the CO₂ flow for acceptors 5 and 18 (marked with stars).

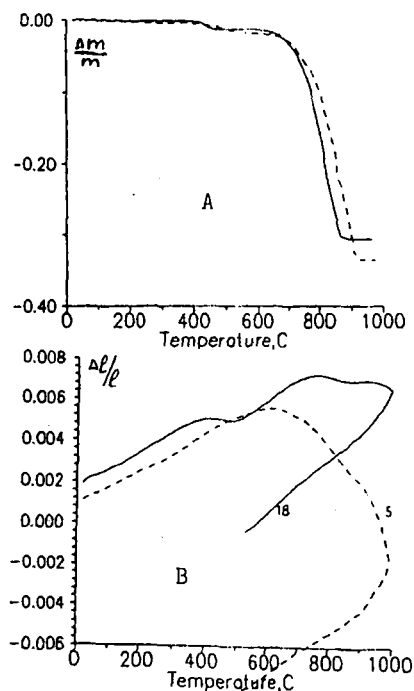


Figure 4. The comparison of the thermo weight (a) and dilatometric (b) curves of the heating and cooling in the air flow for acceptors 5 (dotted line) and 18.